Growth of Cu-1.1at.% Sn and Cu-1.7at.% In Alloy Single Crystals

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Synopsis

Attempts have been made to grow large single crystals of Cu-1.1at.% Sn and Cu-1.7at.% In alloys from the melt by the Bridgman method. Microscopic observation of the chemically etched surfaces and sections of the alloy ingots has shown that they contain a few large grains, if the growing condition is properly chosen, but otherwise they consist of columnar grains. The growth direction of the columnar grains determined by the X-ray Laue method exhibits a slight preference of the <100> and <221> directions for the Cu-Sn alloy and the <111> and <521> directions for the Cu-In alloy. A concentration profile in the grain investigated by EPMA has shown an appreciable fluctuation in as-grown crystals and an annealing in vacuum at 900°C for 100 hr has resulted in a homogenization. The alloy crystals thus heat-treated provide the specimens suitable to LEED studies.

I. Introduction

In the past decades, various attempts have been made to grow single crystals of alloys, which were mostly used for the study of crystal growth[1,2] and mechanical properties[3,4]. Large single crystals are also required to investigate the surface structures of alloys by means of LEED[5,6]. It is important to obtain an information on the growth direction and homogeneity of the large alloy crystals in order to utilize them for the LEED observation. We have made a series of experiments of growing Cu-Sn and Cu-In alloy single crystals and investigated the grain size, the misorientation between neighboring grains and the concentration fluctuation.

The constitution diagrams of Cu-Sn and Cu-In alloys on the copper-rich side are shown in Fig. 1[7]. Both systems have a wide

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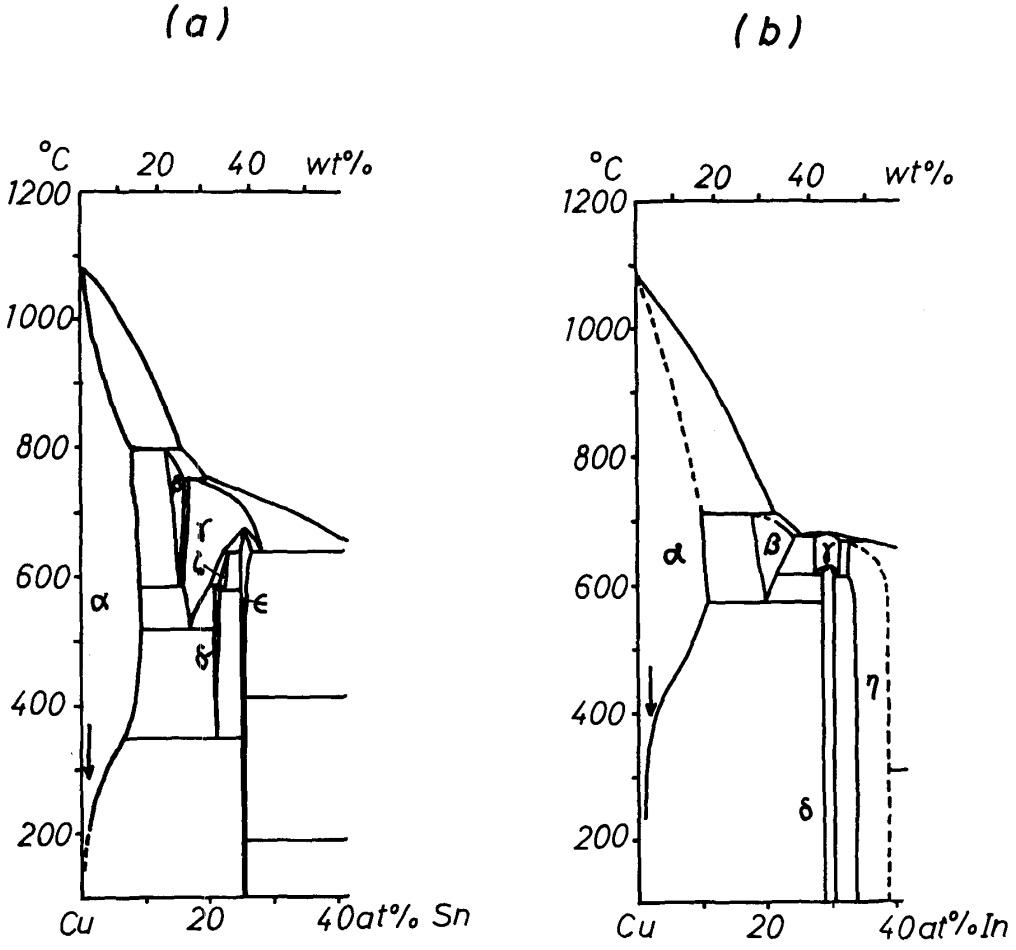

Fig. 1 The constitution diagrams of Cu-Sn and Cu-In alloys on the copper-rich side. Prepared content of solute is indicated by an arrow in the diagram. (a) Cu-Sn system. (b) Cu-In system.

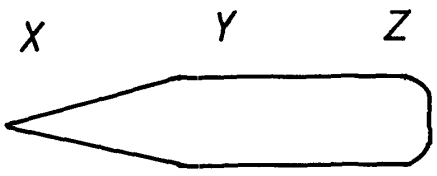

Fig. 2 The three parts of the ingot chemically analyzed. X : bottom, Y : middle, Z : top.

primary solid solution range at high temperature but the range becomes narrow as the temperature falls. This type of alloy is appropriate for the investigation of the precipitation phenomena. An investigation of the crystal growth of such kind of alloys is of particular interest. Two alloys with the compositions of Cu-1.1at.% Sn and Cu-1.7at.% In were prepared in the present study. These compositions correspond to the respective solubility limits of the primary solid solution at room temperature, as indicated by an arrow in Fig. 1. The present paper describes the experimental results including characterization of the large alloy crystals grown.

II. Experimental procedures

The Cu-1.1at.%(2.0wt.%) Sn and Cu-1.7at.%(3.0wt.%) In alloys were prepared from copper(99.998wt.%), tin(99.999wt.%) and indium(99.999wt.%) metals. These materials were melted under argon gas atmosphere. Crystals were grown by the Czochralski(Cz) method in high purity graphite crucible (ash content: $\sim$ 20 ppm) and the Bridgman method in a commercial alumina or a graphite crucible. In the Cz method a seed of pure copper single crystal oriented in the <100> direction was placed in a melt bath held at about 1100°C and pulled out vertically at a rate of 30 mm/hr. Throughout the solidifying process, a concentraion gradient was introduced along the growth direction and the sample diameter was decreased as it grew under a constant condition, so that it was not possible to obtain a sufficiently large single crystal with high solute content by this method. Therefore, we must resort to the Bridgman method.

In this method crystallization was carried out varying growing conditions, such as the melting temperature, the moving velocity and the shape of the crucible. The melt was superheated at temperatures ranging from 1100°C to 1280°C, and the moving velocity was in the range between 1.2 mm/min and 0.2 mm/min. The bottom of the crucible had a cone shape with the apex angle of 60° or 30°. After the melt had been solidified, it was cooled in the vacuum chamber kept at room temperature. Alloy ingots were in the form of a cylinder 12 mm or 14 mm in diameter. Microscopic structures were examined by chemical etching technique in a solution of 10% $(NH_4)_2S_2O_8$ and 90% water. The cross section of the ingot was prepared by mechanical cutting and polishing. Distribution of elements within the grain was examined using an electron probe microanalyzer(EPMA). Determination of the growth direction was carried out by the X-ray Laue method using a pinhole slit 0.5 mm in diameter. Homogenizing treatment of an as-grown crystal by the

Table 1 The local composition of the Cu-2wt.% Sn and Cu-3wt.% In alloy ingots. The notations, X, Y and Z, correspond to the parts of the ingot shown in Fig. 2.

	Cu-Sn (wt.%Sn)	Cu-In (wt.%In)
X	1.55	2.62
Y	1.61	2.84
Z	3.83	4.15

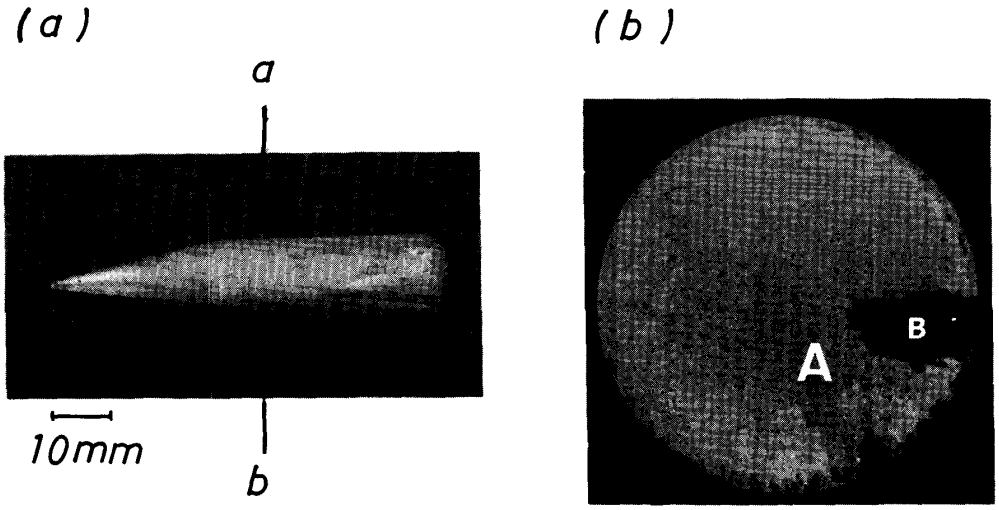

Fig. 3 Photographs of Cu-1.1 at.% Sn alloy crystal grown with the moving velocity 0.2 mm/min. (a) Chemically etched ingot as-grown. The top of the ingot contains a number of grains with small grain size as a result of an increased cooling rate. (b) Chemically etched cross section of the ingot along the line a-b shown in (a).

Bridgman method was made in a vacuum of better than 1×10^{-2} Pa at 900°C for 100 hr and quenched into water.

III. Results

3-1. Concentration gradient along the growth direction

When the melt of the alloy is solidified slowly, concentration gradient is often introduced along the growth direction because the solidification tends to enrich the neighboring liquid in one of its constituents. In order to investigate the concentration gradient, the top, middle and bottom parts of the alloy ingots, shown in Fig. 2, were chemically analyzed. Solute contents of these parts of the Cu-Sn and Cu-In alloys are shown in Table 1. The solute contents are lower in the bottom part which was solidified first and they increase on going from the bottom to the top. In the present study the data on the crystal size and orientation are obtained from the middle part of the ingot, where the composition is not much different from the intended one.

3-2. Microscopic observation

A typical photograph of the Cu-1.lat.% Sn alloy ingot after the chemical etching is shown in Fig. 3 (a). The cross section along the line a-b is shown in Fig. 3 (b). For this alloy, a few large grains having a small misorientation to each other are often observed in the section and tiny grains are observed along the periphery of the ingot as shown in Fig. 3 (b). A photograph of another ingot of the Cu-Sn alloy and its cross section are shown in Fig. 4 (a) and (b), respectively. Three grains are observed in Fig. 4 (b), but there are no tiny grains along the periphery. The grain size is independent of the superheating temperature and moving velocity. The apex angle of the crucible is shown to have an advantage of growing a crystal with large grain size. Figure 5 shows an X-ray Laue pattern obtained from the largest grain C after annealing at about 900°C for 100 hr in vacuum. The pattern was taken with the crystal rotated so that the <110> direction is parallel to the incident beam. It shows that the mosaic spread in the grain is small.

Similar results have been obtained for the Cu-1.7at.% In alloy, but the number of subgrains in the ingot is larger. A typical photograph of the alloy ingot and its cross section along the line e-f are shown in Fig. 6 (a) and (b), respectively. The grains F_1, F_2, F_3 and F_4 shown in Fig. 6 (b) are the subgrains which have crystallographic

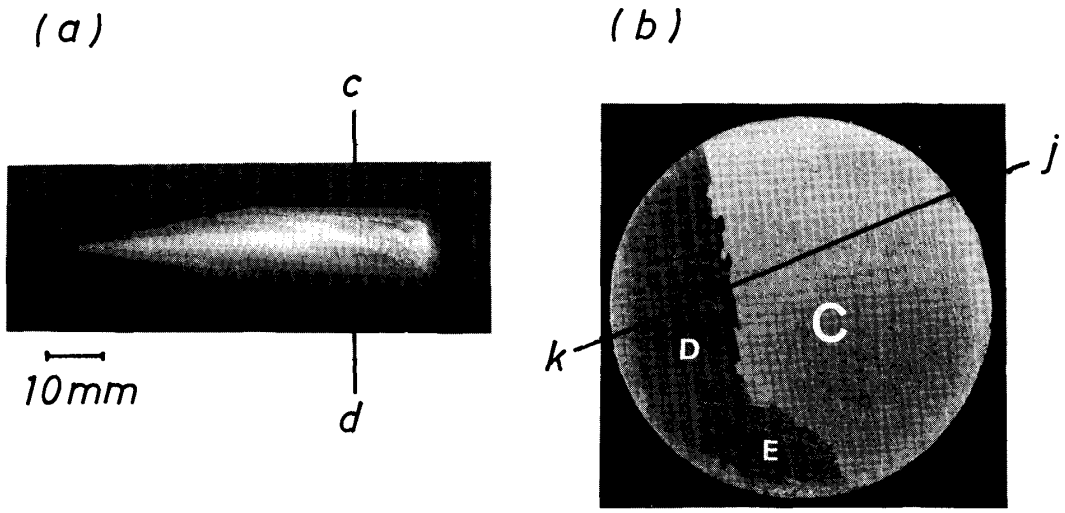

Fig. 4 Photographs of Cu-1.1 at.% Sn alloy crystal grown with the moving velocity changed in three steps of 0.2, 0.5 and 1.2 mm/min. (a) Chemically etched ingot as-grown. (b) Chemically etched cross section of the ingot along the line c-d shown in (a).

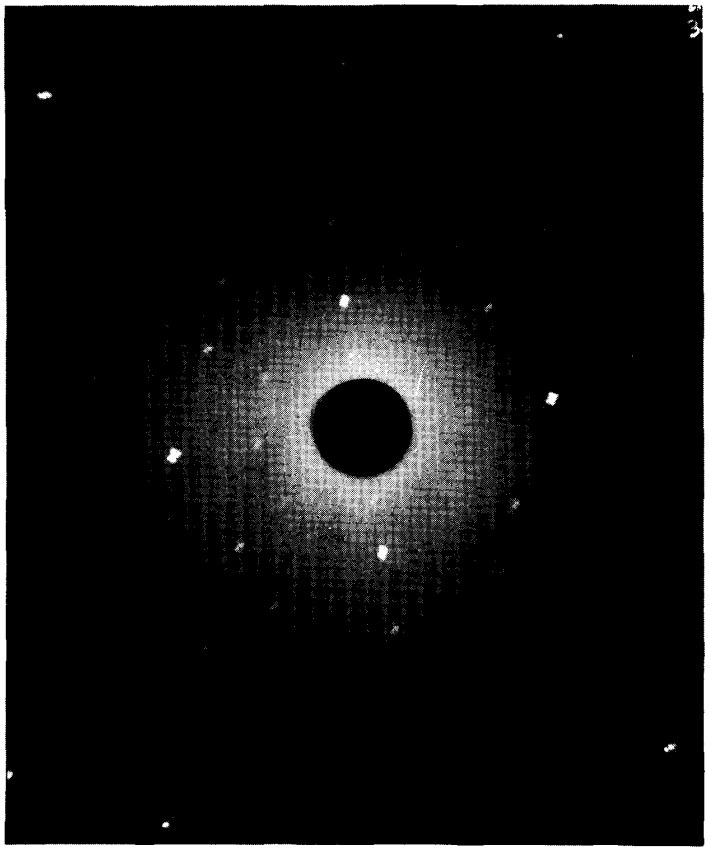

Fig. 5 Laue photograph of the grain C shown in Fig. 4 (b). The crystal is rotated so that the <110> direction of the grain coincides with the incident beam direction.

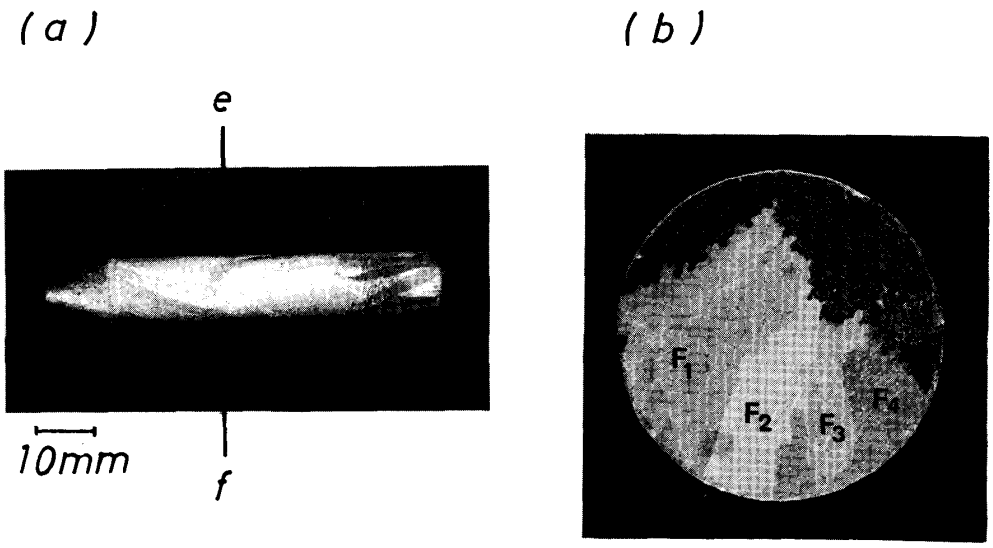

Fig. 6 Photographs of Cu-1.7 at.% In alloy crystal grown with the moving velocity 0.3 mm/min. (a) Chemically etched ingot as-grown. (b) Chemically etched cross section of the ingot along the line e-f shown in (a).

misorientation within a few degrees to each other. A photograph of another ingot of the Cu-In alloy and its cross section are shown in Fig. 7 (a) and (b), respectively. Figure 8 shows an X-ray Laue pattern obtained from the largest grain H after the heat treatment. The sharpness of the diffraction spots indicates the high quality of the crystals grown.

It is shown that growing large single crystals is more difficult for the Cu-In alloy than for the Cu-Sn alloy. The solute content in the solid solution seems to be an important factor for growing large alloy single crystals. This tendency was recognized in the case of a Cu-0.59at.% Ag alloy which was grown by the Cz method[8].

3-3. Stereographic projection of the growth direction

Distribution of the growth direction in the alloy crystals is expressed in the stereographic triangle. The growth direction of the grains A and B of the Cu-1.1at.% Sn alloy in Fig. 3 (b) is plotted in Fig. 9 (a). It is shown that the grain B is a subgrain of A. The growth direction of the three grains in the section shown in Fig. 4 (b) is plotted in the stereographic triangle in Fig. 9 (b). A large circle represents the largest grain C. It is shown that the grains C and D have nearly identical crystallographic orientation and the grain E has an orientation much deviating from it. Ten grains in the four ingots

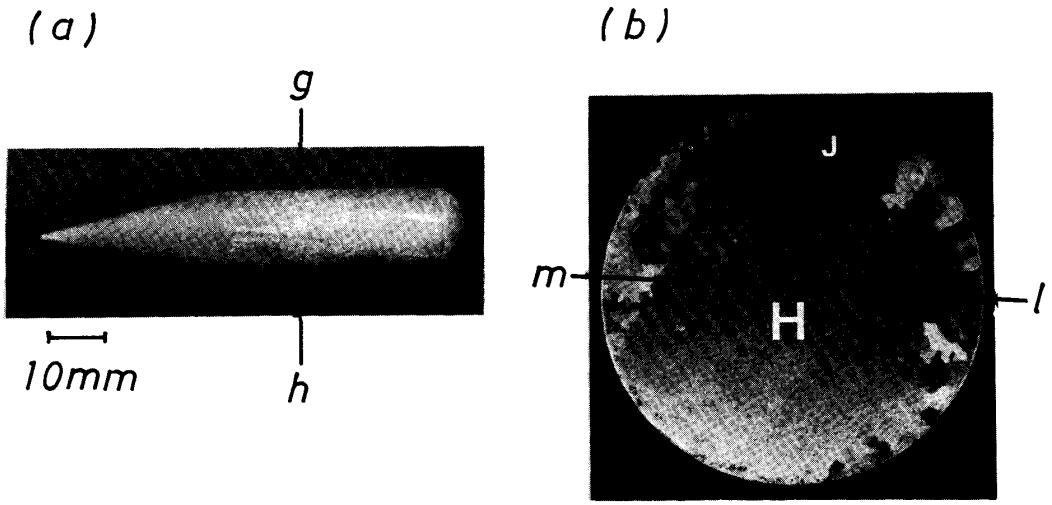

Fig. 7 Photographs of Cu-1.7 at.% In alloy crystal grown with the moving velocity 0.4 mm/min. (a) Chemically etched ingot as-grown. (b) Chemically etched cross section of the ingot along the line g-h shown in (a).

Fig. 8 Laue photograph of the grain H shown in Fig. 7 (b). The crystal is rotated so that the <100> direction of the grain coincides with the incident beam direction.

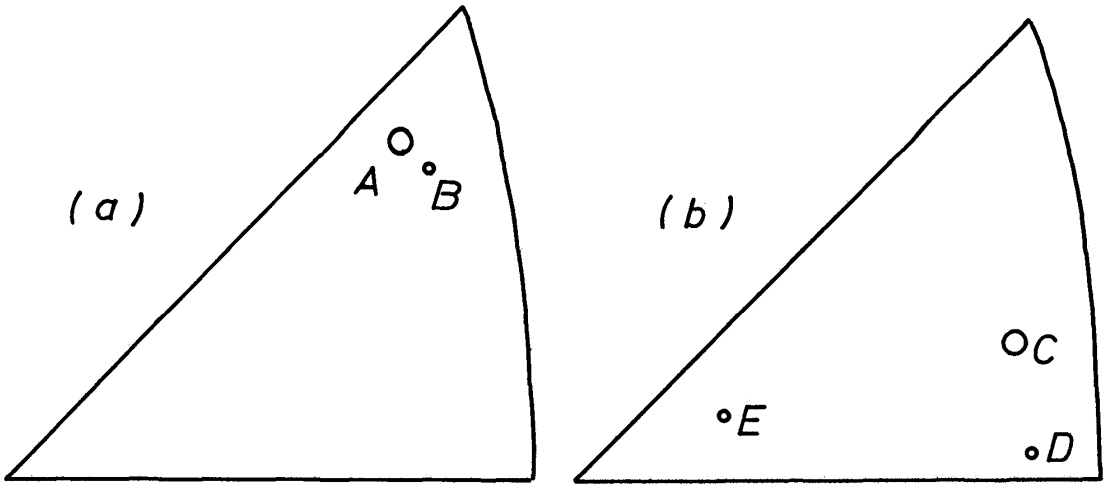

Fig. 9 Stereographic projections of the growth directions of the grains in the Cu-1.1 at.% Sn alloy ingot. (a) Stereographic projection for the grains shown in Fig. 3 (b). A large circle corresponds to the largest grain A. (b) Stereographic projection for the grains shown in Fig. 4 (b).

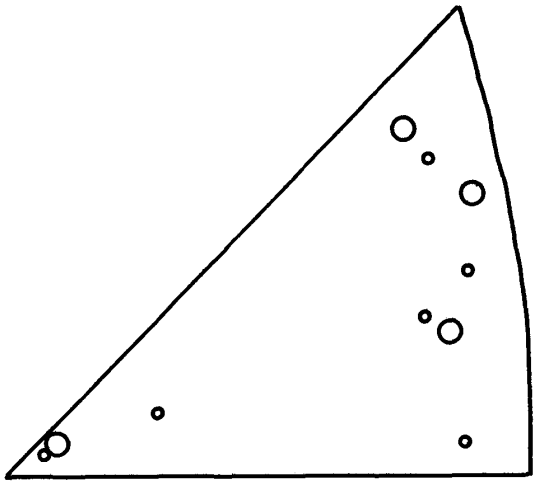

Fig. 10 Stereographic projection of the growth directions of the grains observed in the four Cu-Sn alloy ingots.

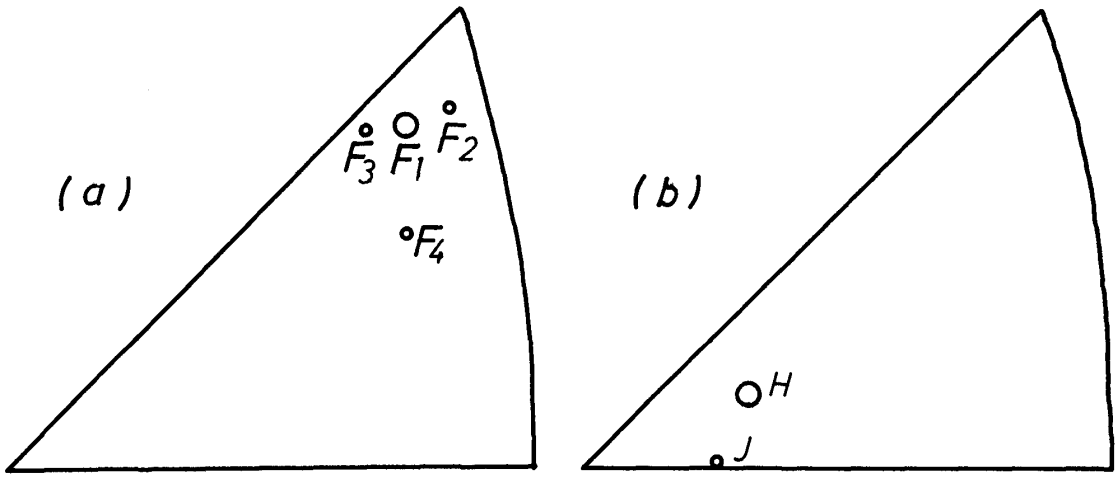

Fig. 11 Stereographic projections of the growth directions of the grains in the Cu-1.7 at.% In alloy ingot. (a) Stereographic projection for the grains shown in Fig. 6 (b). A large circle corresponds to the largest grain F_1. (b) Stereographic projection for the grains shown in Fig. 7 (b).

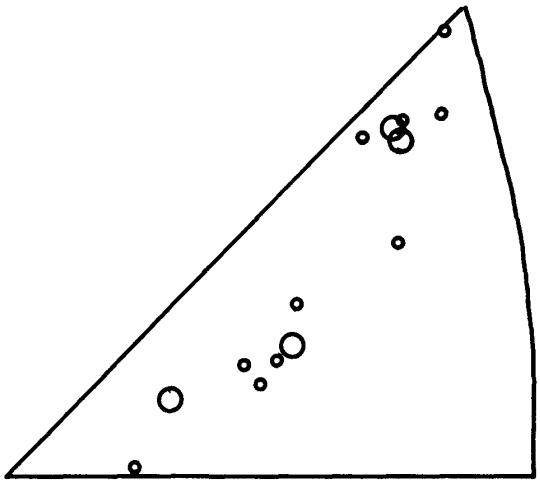

Fig. 12 Stereographic projection of the growth directions of the grains observed in the four Cu-In alloy ingots.

of the Cu-Sn alloy were X-rayed and the results are plotted in Fig. 10. In this alloy, the growth direction of the grains exhibits a slight preference of the <100> and <221> directions.

For the Cu-1.7at.% In alloy the four grains shown in Fig. 6 (b) and two grains H and J in Fig. 7 (b) were X-rayed and the results are plotted in Fig. 11 (a) and (b), respectively. The former group of grains have a nearly identical crystallographic orientation close to the <111> pole. On the other hand, the latter grains have a crystallographic orientation close to the <521> pole. Fourteen grains in the four ingots of the Cu-In alloy were also X-rayed and the results are plotted in Fig. 12. The growth direction of the grains also exhibits a slight preference of the <111> and <521> directions, and there are no grains with the <110> orientation.

It has been shown[9] that fcc metals generally have columnar grains with their <100> axis parallel to the direction of heat flow. However, no marked <100> preferred orientation of the grains is observed here for the Cu-Sn and Cu-In alloy crystals. This is probably due to the relatively short growth length compared with the large diameter of the crucible and, if the crystals with increased length were grown, they would exhibit a perfect <100> orientation of a single grain.

3-4. Homogeneity of the alloy crystal

Concentration fluctuation in a grain of alloy crystals may be introduced during the solidification. The concentration fluctuation in the grain of the Cu-1.lat.% Sn and Cu-1.7at.% In alloy crystals was investigated by EPMA. Figure 13 (a) shows the concentration profiles of copper and tin in the Cu-Sn alloy crystal. Scanning was made in the grains C and D along the line j-k shown in Fig. 4 (b). Appreciable fluctuation of the tin content is observed along the line, but no evidence of the precipitation of the ε phase[7] is detected in the interior of the grains as well as at the grain boundary within the limit of EPMA sensitivity. It seems that the fluctuation has occurred during the solidification from the melt. After annealing the alloy crystal at 900°C for 100 hr, the concentration fluctuation disappears as shown in Fig. 13 (b). Similar results have been obtained for the Cu-In alloy crystal. Figures 14 (a) and (b) show the concentration profiles of copper and indium by EPMA before and after the annealing at 900°C for 100 hr, respectively. The scanning was made along the line l-m in the section of the ingot shown in Fig. 7 (b). In the profile of Fig. 14 (a) an extremely high peak of indium is observed, indicating that the In-rich phase, probably the δ phase,

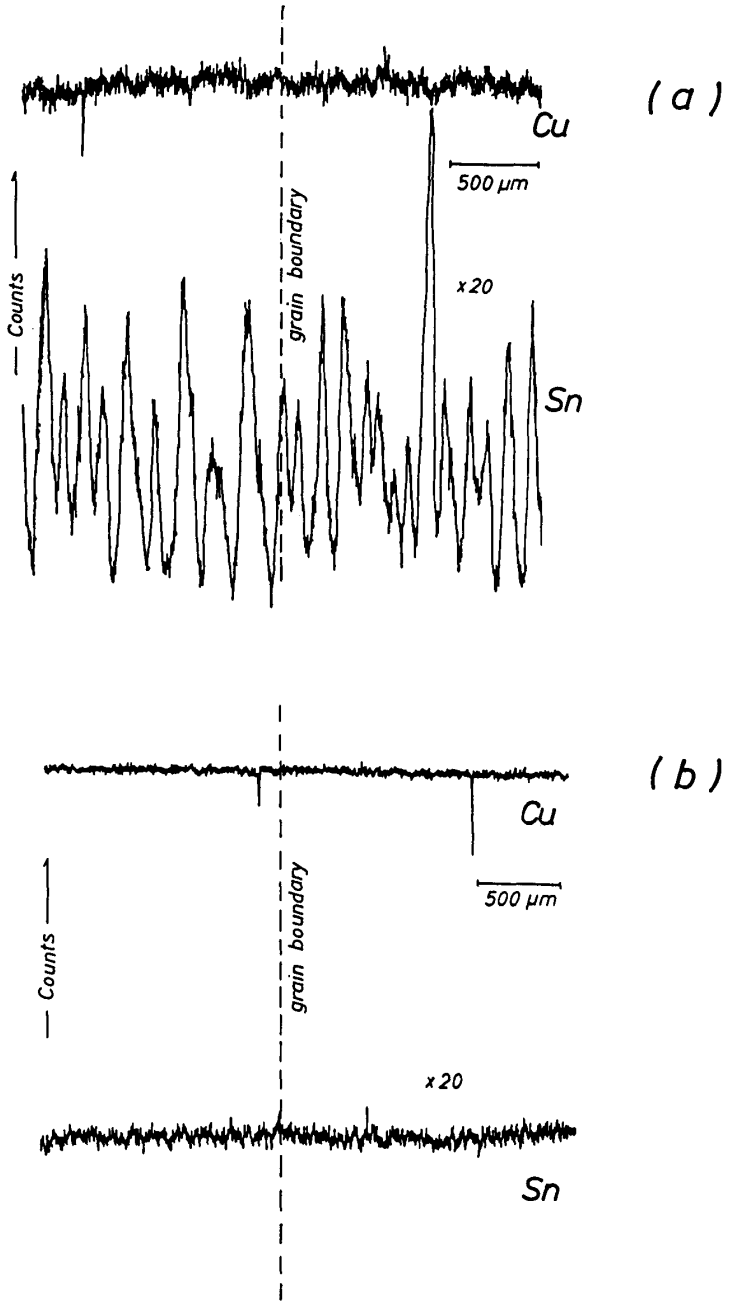

Fig. 13 Characteristic X-ray profile obtained by using EPMA from the surface of the Cu-1.1 at.% Sn alloy. Cu Kβ and Sn Lα radiation. This is a part of the profile scanned through the section of the ingot along the line j-k shown in Fig. 4 (b). (a) As-grown. (b) Annealed at 900°C for 100 hr in vacuum.

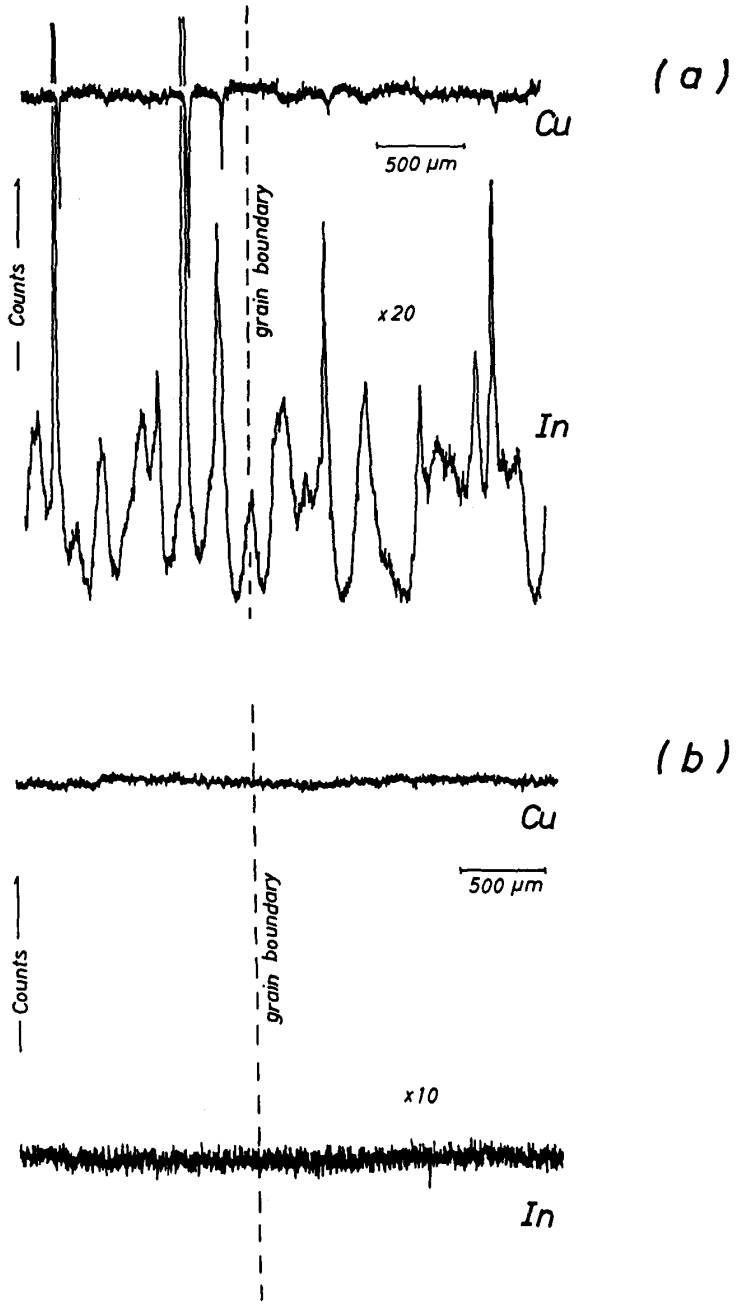

Fig. 14 Characteristic X-ray profile obtained by using EPMA from the surface of the Cu-1.7 at.% In alloy. Cu Kβ and In Lα radiation. This is a part of the profile scanned through the section of the ingot along the line l-m shown in Fig. 7 (b). (a) As-grown. (b) Annealed at 900°C for 100 hr in vacuum.

has precipitated. However, after the heat treatment the concentration distribution becomes homogeneous.

IV. Discussion

In the present work, it has been not possible to grow a perfect single crystal of the Cu-Sn and Cu-In alloys. However, the growing conditions adopted, i.e. the superheating temperature, moving velocity and apex angle of the crucible, have been shown to be appropriate for growing large grains and therefore a much increased length of the ingot will lead to the formation of the perfect alloy single crystal at its top.

A clean (100) surface of the Cu-1.lat.% Sn alloy crystal grown in the present work was prepared by the same method used in the case of pure copper[10] and the LEED pattern has been observed. Figure 15 shows a series of LEED patterns as a function of the accelerating voltage of electrons. The patterns correspond to a $(\sqrt{2} \times 3\sqrt{2})R45°$ structure which is due to a reconstruction induced by tin dissolved in copper. These LEED patterns are observed in a wide region of a grain without tilting the crystal. Diffraction spots are sharp and intense. These results mean that the single crystal obtained by the present method is of a good quality and fully used for the study of the surface structure of the alloys.

Aknowledgment

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References

(1) A. Rosenberg and W.A. Tiller, Acta Met., 5 (1957), 565.
(2) S. Hayashi and J. Echigoya, Kristall and Technik, 13 (1978), 657.
(3) E. Kuramoto and H. Suzuki, Trans JIM., 17 (1976), 683.
(4) H. Suga and T. Imura, Trans JIM., 17 (1976), 605.
(5) H.C. Potter and J.M. Blakely, J. Vacuum Sci. Technology, 12 (1975), 635.
(6) V.S. Sundaram, B. Farrell, R.S. Alben and W.D. Robertson, Phys. Rev. Letters, 31 (1973), 1136.

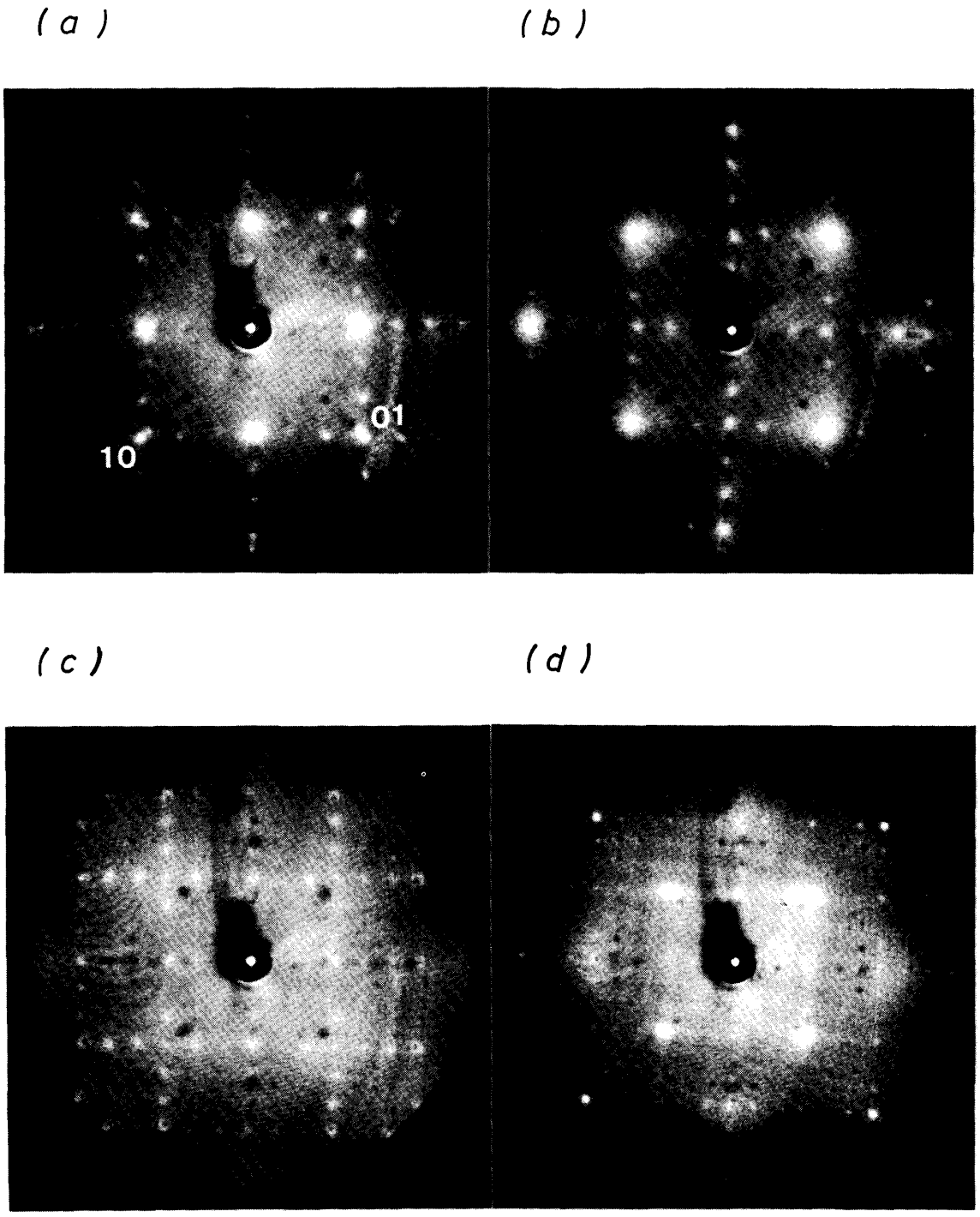

Fig. 15 LEED patterns observed from the (100) surface of the Cu-1.1at.% Sn alloy crystal grown in the present work. Accelerating voltage; (a): 100 V, (b): 120 V, (c): 160 V, (d): 220 V.

(7) M. Hansen and K. Anderko, Constitution of Binary Alloy, 2. Ed. by McGraw-Hill, New York, (1958), 591, 634.
(8) Y. Fujinaga, T. Miura and H. Iwasaki, unpublished.
(9) C.S. Barrett and T.B Massalski, Structure of Metals, 3. Ed. by McGraw-Hill, New York, (1966), 535.
(10) Y. Fujinaga, Surface Sci., 64 (1977), 751.